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MASS SPECTROMETRIC STUDIES OF REACTIONS IN FLAMES -
QUANTITATIVE SAMPLING OF FREE RADICALS
FROM ONE-ATMOSPHERE FLAMES

TECHNICAL REPORT
16 July 1965

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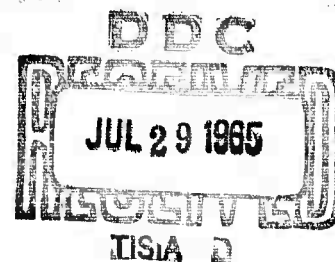Program Code No. 4910

MRI Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington, D. C.

MIDWEST RESEARCH INSTITUTE

425 VOLKER BOULEVARD/KANSAS CITY, MISSOURI 64110/AC 816 LO 1-0202

MASS SPECTROMETRIC STUDIES OF REACTIONS IN FLAMES -
QUANTITATIVE SAMPLING OF FREE RADICALS
FROM ONE-ATMOSPHERE FLAMES

by

Thomas A. Milne
Frank T. Greene

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16 July 1965

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ABSTRACT

Direct mass spectrometric sampling studies of one-atmosphere flames are described. A simple model of the sampling process is summarized which accounts for the effects and results obtained. Stable product analysis and evidence for appreciable temperature dependence of fragmentation patterns are shown. Quantitative sampling of the free-radicals H, O, OH and Cl from the burnt gas region of one-atmosphere flames is demonstrated, with direct observation of excess free radical concentrations in the reaction zones of these flames.

I. INTRODUCTION

The first paper[1] in this series described the relationship between aerodynamic molecular beam formation and the problem of the direct mass spectrometric sampling of systems at atmospheric pressure and above. The experimental dependence of the beam intensity was given as a function of various system parameters, and the mass separation effect was quantitatively evaluated.

Since the publication of that paper, considerable theoretical and experimental work on the free jet expansion and aerodynamic molecular beams has been reported. Now a rather simple model of the sampling process can be formulated which accounts for the observed effects and gives a quantitative history of the sampling process. In this paper, we summarize this model and present data on beam effects and on the sampling of reactive species from 1-atmosphere flames.

II. BEAM FORMATION FROM HIGH-PRESSURE SOURCES

Starting from a stagnant condition, the gas to be sampled is accelerated as it approaches the sampling orifice, and reaches the speed of sound near the throat of the orifice. At this point, the pressure has dropped by as much as 15-20 per cent. From the sonic condition, the gas expands very rapidly as a "free" or supersonic jet. Along the center line of the jet, the expansion is essentially isentropic, reaching a nearly collisionless flow regime in a distance of 10-20 orifice diameters downstream. If the second slit (skimmer) is placed well downstream of the transition to "collisionless" flow, then shock phenomena are unimportant, and the attenuation experienced by the beam can be accounted for by self-scattering in the beam and by scattering from background gas between the orifice and the detector.

The justification for this model has been discussed in several recent publications. The ideal expansion history downstream of the sonic orifice can be calculated by means of the Mach number vs. distance calculations of Sherman[2] for various ratios of heat capacity, γ. Fenn et al.,[3] have verified these Mach number predictions over a fairly wide range of conditions and discussed various aspects of beam behavior and attenuation. The authors have discussed sampling history, scattering behavior, partial condensation effects and some preliminary sampling results in two recent symposia.[4,5] Scott[6] has measured velocity distributions in aerodynamic beams to provide a more detailed picture of the expansion; Deckers and Valleau[7] have discussed effects associated with collisions in the beam, and the Karlssruhe group

continues to work on various aspects of beam formation.[8] This work and the work of many others, of pertinence to the sampling problem, is extensively reviewed by Knuth.[9]

The effects upstream of the orifice are less well understood. No analytical solution exists for the subsonic flow upstream of the orifice. A point sink model has been used with linear interpolation near the orifice to represent the subsonic flow. The results of these calculations are in satisfactory agreement with the more recent experimental data of Sherman.[2] The subsonic and low Mach number supersonic flow, which is sensitive to the orifice geometry, may be the most critical for the quenching of very rapid equilibria.

A quantitative temperature pressure history of the expansion can be obtained from the combined subsonic and supersonic calculations. This history is given in previous publications.[4,5] For a monatomic gas at 2000°K and 1 atm., expanding through a 0.125-mm. orifice, the translational temperature drops to 30°K and the pressure to 10^{-5} atm. within about 1.5 μsec. from the first appreciable change. Gases with larger heat capacities will expand somewhat more slowly.

This simple, ideal picture of the sampling process, although it cannot be completely correct, should not be substantially wrong. It appears from the calculated history of expansion that a reaction with a positive activation energy will be satisfactorily quenched.[4] Reactions with negative temperature coefficients will be quenched only by the drop in collision frequency, as shown by the partial condensation effects observed.[10,11] Real sampling situations may involve other factors. When sampling flames, one must consider the effects of flame-probe interactions, of reactions during sampling, and of γ changing with temperature. The combined effects can, therefore, best be tested by sampling flames of various kinds for species present in known equilibrium concentration. Some experiments of this type are described below.

III. EXPERIMENTAL

The beam-sampling system, which uses a Bendix mass spectrometer[12] as a detector, is identical to that described in Part I[1] and in Refs. 4 and 5, except that a beam "chopper" with a phase-sensitive detection system has been substituted for the mechanical shutter. A magnetically driven vibrating reed periodically interrupts the beam. Princeton Applied Research lock-in amplifiers provide phase-sensitive detection of the modulated beam. Details will be given in a separate article. Modulation at either 10 or 50 cps gave

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identical results, indicating that within experimental error, no appreciable scattered or random gas was being modulated. Although molecules from the modulated beam scattered directly into the electron beam would not be distinguished by the frequency change, we believe that for our geometry this is not a significant source of signal. In a comparison of ratios of reactive to stable species in flames, such as O/O_2, results taken with the manual shutter gave a smaller ratio of O/O_2 than with the modulated beam. This observation confirms earlier evidence that the shutter-dependent signal obtained with the manual shutter contains an appreciable component due to gas scattered from the beam in the ion source.

With the present system the background-to-beam discrimination is about 1,000 for moderately strong peaks. That is, one should be able to detect a beam signal which is 0.1 per cent of an interfering background peak. This figure was estimated on the basis of the peak-to-peak noise from various strength background peaks, assuming a S/N of 1.0. As one check on the discrimination ratio, a weak beam of argon was created by adding about 4 per cent argon to a stoichiometric $CO-O_2$ flame being sampled. The argon beam was then monitored while argon was leaked directly into the ion source. By the time the total argon signal had reached 1,000 times the original beam intensity, the argon beam intensity had dropped about 30 per cent, presumably because of the rather high argon pressures in the ion source.

Simple sheathed burners and torch flames have been used in the work described here. Some survey experiments, for which adiabatic flame temperatures were sufficiently accurate, employed either laboratory torches or simple tubes fed with premixed gases. For more careful work, sheathed burners were constructed from bundles of 20 gauge stainless steel tubes, capillary glass tubes, or cylindrical rolls of corrugated shim stock. Direct temperature measurements were made by standard line reversal techniques. The measured temperatures were generally from 50 - 100°K below the adiabatic temperatures. These sheathed flames gave convenient, flat flames for work in the burnt gas region. Because of the poor spatial resolution resulting from the large sampling orifices and very thin reaction zones, probing into the reaction zone of any of these 1-atm. flames led to only qualitative profiles.

The sampling orifices used were 90° cones spun from 0.12 and 0.024-mm. thick Pt-20 Rh sheet with 0.24 mm. diameter holes drilled in the apex. The relatively large orifices were used in anticipation of work with condensable species, where plugging is a problem. Although the orifices were soldered to a water-cooled plate, the tips of the orifices were white hot and not far from their softening points with the hotter H_2-O_2 and CH_4-O_2 flames.

IV. SAMPLING FROM ONE-ATMOSPHERE FLAMES

To test empirically the ability of the direct sampling technique to quench reactions and to assess the major difficulties involved, a number of convenient flame systems were surveyed without making a detailed study of any of them. The criterion for quantitative sampling adopted was that the measured equilibrium constant for the reactions being studied agree within a factor of two with the literature values, which were calculated from data taken from the JANAF Tables.[13] Experimental errors of this magnitude are usually to be expected for third-law mass spectrometric studies due to lack of knowledge of (a) mass spectrometer transmissions, (b) collection efficiencies and (c) ionization cross sections. Results are presented for stable products, free radicals and temperature-dependent fragmentation patterns.

A. Stable Products and Temperature-Dependent Fragmentation Patterns

A number of flames were sampled for the stable products H_2, O_2, H_2O, CO and CO_2. Several CH_4-O_2-AR and CO-O_2 sheathed flames were probed as a function of distance from the reaction zone. Temperatures were measured by line reversal for these flames. A few of the results reported in Ref. 4 are repeated in Table I for comparison. Stable species were measured in many other flames but have not been reduced to equilibrium constants, since the above data seemed to be sufficiently satisfactory to warrant going on to the more critical test of sampling very reactive species.

TABLE I

EQUILIBRIUM CONSTANTS DETERMINED FROM STABLE PRODUCT ANALYSES IN SEVERAL FLAMES SAMPLED DIRECTLY AT ONE ATMOSPHERE

Flame Composition (Mole Ratios)				Exptl. Temp. (°K)	K_{eq}	
					Exptl.	Calc.
CH_4	CO	O_2	Ar		$H_2 + 1/2\ O_2 \longrightarrow H_2O$	
1		2	8	2454	234	210
1		2.4	8	2457	151	210
					$CO + 1/2\ O_2 \longrightarrow CO_2$	
1		2	8	2454	36.4	36.0
1		2.4	8	2457	28.9	36.0
	1	1		2769	4.9	7.6
	4	3		2824	4.5	6.0
	2	1		2834	4.8	5.7
	3	1		2807	4.4	6.4

Two points of interest emerged from these stable product data. First, agreement was obtained for the H_2 concentrations only after applying the first power of the molecular weight correction established in Part I of this series.[1] There is nothing in the simple model of the mass separation effect to indicate a temperature dependence, and none has been observed.[1] For the H_2 data in CH_4-O_2-Ar flames, the correction relative to O_2 is a factor of 16, the observed H_2^+ peak thus being rather weak.

One complication which arose in making the stable flame product measurements was the temperature-dependence of the fragmentation patterns of even these relatively small molecules. It was first observed that, with an ionizing electron energy of 50 ev., the fragmentation of CO_2 to CO^+ was appreciably temperature-dependent. This temperature-dependence became apparent when the $44^+/28^+$ ratio for a series of progressively leaner flames reached a limiting value. Two experiments were performed to determine the magnitude of this change. CO_2 was added to a lean H_2-O_2 flame which burned at about 1950°K. Since there is a negligible quantity of CO in this lean flame at equilibrium, the 28^+ observed at 50 ev. can be assigned to the fragmentation of hot CO_2. Entrainment of N_2 was shown to be negligible. An approximately constant value of $44^+/28^+$ was obtained over the first three centimeters beyond the visible reaction zone, indicating equilibration of the reaction $CO_2 + 1/2O_2 \rightleftharpoons CO_2$. The results showed that the fragmentation of CO_2 to CO^+ varies from about 12 per cent at room temperature to 17 per cent at 2000°K in our instrument.

A similar magnitude of temperature effect was deduced from the $44^+/28^+$ ratios observed at 25 and 50 ev. in the four CO-O_2 flames shown in Table I. Fragmentation was negligible at 25 ev. and yielded a CO_2/CO ratio in good agreement with equilibrium calculations. The 50 ev. data could then be corrected for the CO contribution to 28^+ and the hot CO_2 cracking patterns determined.

Another test of the effect of temperatures on fragmentation patterns was provided by sampling HCl from a series of rich H_2-O_2-N_2 flames which have been extensively studied by Sugden.[14] Profiles of $36^+/35^+$ (at an ionizing energy of 50 ev.) in the burnt gas regions of two such flames are shown in Fig. 1, together with measured flame temperatures and the room temperature value of $36^+/35^+$ for pure HCl. A third flame, F_5 in Sugden's nomenclature, exhibited behavior intermediate between U_5 and F_3.

Two things should be noted. First, the limiting value of the $36^+/35^+$ ratio, well removed from the reaction zone, is smaller than for cold HCl and decreases when flame temperature increases. The HCl/Cl equilibrium ratio is very large for even the hottest of these flames, and hence the limiting $36^+/35^+$ should represent the fragmentation patterns of HCl at these temperatures. This apparent effect of temperature on HCl fragmentation is
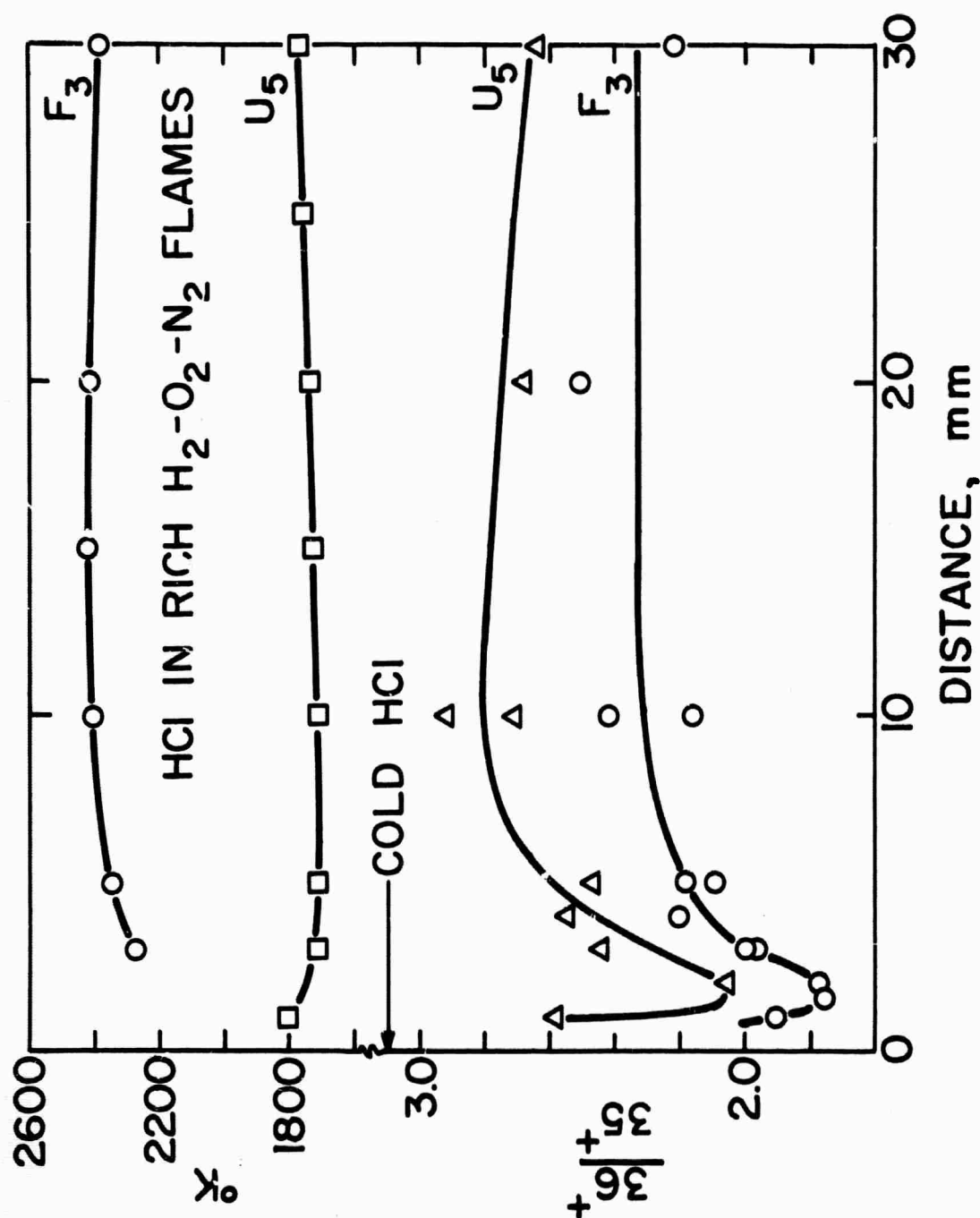
Fig. 1 - Line Reversal Flame Temperatures and Chlorine-Containing Species Profiles in Two Rich, H_2-O_2-N_2 Flames Directly Sampled at One Atmosphere

comparable to the effect on CO_2. Temperature effects _can_ be significant, even for relatively small molecules, and could seriously affect results with unknown systems. Flames could conceivably be convenient media in which to study such effects.

There is not contradiction between the observations of high-temperature fragmentation effects and the claim that the flame gases are cooled extremely during beam formation,[4] since, in the latter case, reference is to translational temperatures. Translational, rotational and vibrational degrees of freedom do not equilibrate to the same extent during the expansion. As a first approximation, it is assumed that there is no vibrational relaxation in such rapid expansion, but that extensive rotational relaxation and nearly perfect translational relaxation[3,6] occur. Thus, the translationally and rotationally cold CO_2 and HCl are still vibrationally hot, rnd it is probable that the populations of the vibrational levels control the fragmentation behavior. The temperature-dependence of fragmentation could conceivably provide a rough way of detecting large changes in vibrational temperatures in partly equilibrated expansions. One would want to choose larger molecules with larger temperature effects, however.

B. Reactive Species

Another point of interest in Fig. 1 is the marked drop in the $36^+/35^+$ ratio as the reaction zone is approached in these flames. Since the temperature is decreasing toward the reaction zone (the apparent increase in Flame U_5 of Fig. 1 is due to chemi-excitation effects), this drop can only be interpreted as being due to a significant Cl atom concentration. The abrupt rise in the $36^+/35^+$ ratio at small distances occurs when the flame suddenly visibly attaches to the cool sampling probe, and the unburned gas mixture is being sampled. Sugden has argued that in this type of flame the reaction $H + HCl \rightleftharpoons H_2 + Cl$ will be much more quickly equilibrated than the recombination of the excess of H atoms known to be present in the reaction zone.[15] We can use the observed $36^+/35^+$ ratios, after correction for fragmentation, to deduce the HCl/Cl ratio at each point in the flame. Knowing H_2 in these rich flames by measurement or calculation, one can calculate the H atom concentration. As previously mentioned, Fig. 1 should only be interpreted qualitatively because of the large cooled orifice which is used and the very narrow reaction zone at 1 atm. Nevertheless, it is of interest to compare the calculated ratio of $[H]/[H]_{eq}$ for several of these flames. Maximum ratios of 17, 320, 446 and 4,000 were calculated for the progressively cooler flames, F_3, F_5, U_5, and U_8, respectively. These values are comparable to determinations made by spectroscopic means,[16] and give qualitative support to the validity of the direct sampling scheme.

In addition to the Cl atom measurements shown above, the equilibrium $Cl_2 \rightleftharpoons 2Cl$ was studied in several cool $CO-O_2-Ar$ flames. The results, reported in Ref. 4, agreed with literature values to within a factor of two.

The most demanding test of quenching was felt to be the quantitative sampling of the species O, OH, and H. Oxygen atoms were studied first in $CO-O_2$ and H_2-O_2 flames identical to those in Table I. At 50 ev. ionizing electron energy, fragmentation of CO_2 and O_2 to O completely swamped the 16^+ from O atoms. At a nominal 20 ev. and at room temperature the fragmentation of CO_2, CO, and O_2 to O^+ was negligible. In view of the simultaneous uncertainties in ability to sample O atoms and the suspected temperature-dependent fragmentation of O_2, CO_2, H_2O, or CO, the correlations of the O^+ data from the several flames with the equilibrium calculations provide the best evidence that fragmentation was negligible at 20 ev. Table II shows the results for the four $CO-O_2$ flames studied.

TABLE II

OXYGEN DISSOCIATION EQUILIBRIA MEASURED BY DIRECT SAMPLING
OF SEVERAL $CO-O_2$ FLAMES AT ONE ATMOSPHERE

Flame Composition (Mole Ratios)		Exptl. Temp. ($°K$)	$O \longrightarrow 1/2\ O_2$	
			Exptl.	Calc.
CO	O2		K_{eq}	
1	1	2769	24.5	20.4
4	3	2824	22.0	15.9
2	1	2834	22.5	15.1
3	1	2807	20.9	17.0

Figure 2 gives typical profiles in one of the flames. The effects of entrainment are noted at large distances while the excess O atoms near the reaction zone are a prominent feature. The partial pressures of oxygen atoms were determined to vary from 0.01 to 0.025 atm., assuming equal atom and molecule cross sections at 20 ev.[17] and making a mass separation correction. The equilibrium constants are in quite satisfactory agreement at the measured flame temperatures.

Oxygen atoms were also sampled from several $H_2-O_2-N_2$ flames burned on simple torch tips. The results are shown in Table III together with the adiabatic flame temperatures. The agreement between measured and calculated atom partial pressures is quite good over large differences in the O_2/O equilibrium ratios in the lean and stoichiometric flames. The excess O atom
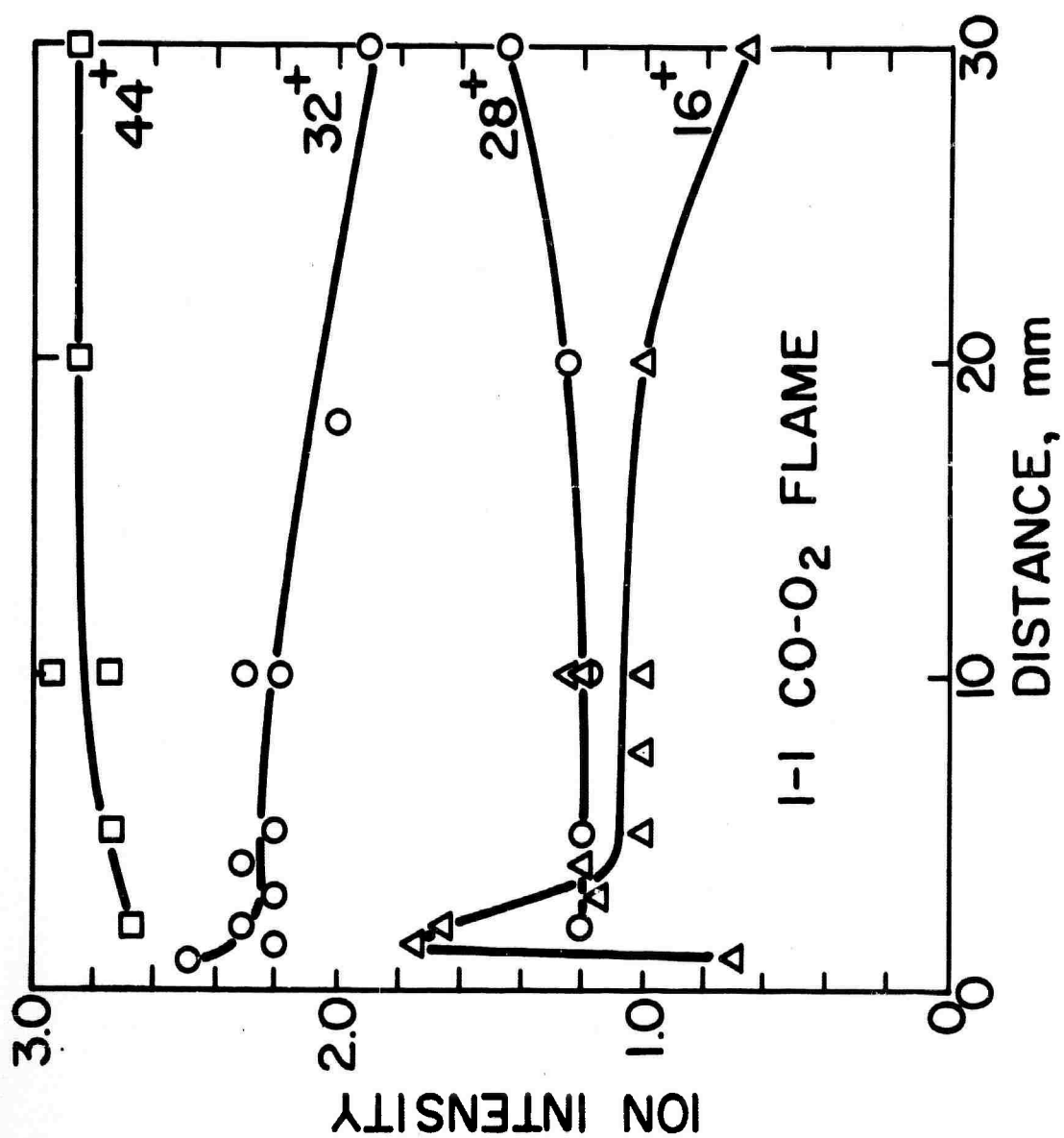
Fig. 2 - Species Profiles in a Lean CO-O₂ Flame Directly Sampled at 2770°K and One Atmosphere

concentrations observed could well be due to incomplete equilibration since profiles were not taken in the torch experiments. A more careful study, including profile and temperature measurements, was made for the 2-4 flame using a sheathed burner. The O/O_2 ratio was very nearly the same as that shown in Table II. The O atom profile through the 2-4 flame is shown in Fig. 3.

TABLE III

OXYGEN ATOMS SAMPLED DIRECTLY FROM SEVERAL
ONE-ATMOSPHERE H_2-O_2-N_2 FLAMES

Flame Composition (Mole Ratios)			Adiabatic Flame Temp. (°K)	Partial Pressures in %			$O \longrightarrow 1/2\ O_2$ K_{eq}	
				O		O_2		
H_2	O_2	N_2		Exptl.	Lit.	Lit.	Exptl.	Calc.
2	1	1	2889	1.6	1.3	2.7	10.1	13.2
2	3		2720	3.3	2.8	ca 50.0	21.3	25.6
2	1	2	2709	0.8	0.5	1.5	16.1	27.0
2	4		2570	2.4	1.6	ca 60.0	32.3	50.0

Hydroxyl radicals were sampled from an even greater variety of flames, with varying temperatures and mixture ratios, than were oxygen atoms. The same problems exist for OH determinations as for O due to lack of knowledge of the high temperature fragmentation of H_2O to 17^+. The results from a number of flames burned on a simple torch tip are shown in Table IV. The $18^+/17^+$ ratios at 50 ev. show virtually no temperature or composition dependence and are in agreement with the $18^+/17^+$ ratio from pure water at room temperature. If the temperature dependence of fragmentation is the same at 20 ev. as at 50 ev., then H_2O makes . negligible 17^+ contribution at 20 ev. in these flames. The 20 ev. ratios of $18^+/17^+$ correlate rather well with the equilibrium values as shown in the last two columns and indicate quantitative sampling of OH radicals.

In the four flames of Table IV for which O atom data were reported, the equilibrium $H_2O+O \rightleftharpoons 2OH$ could be tested. The results are given in Table V.
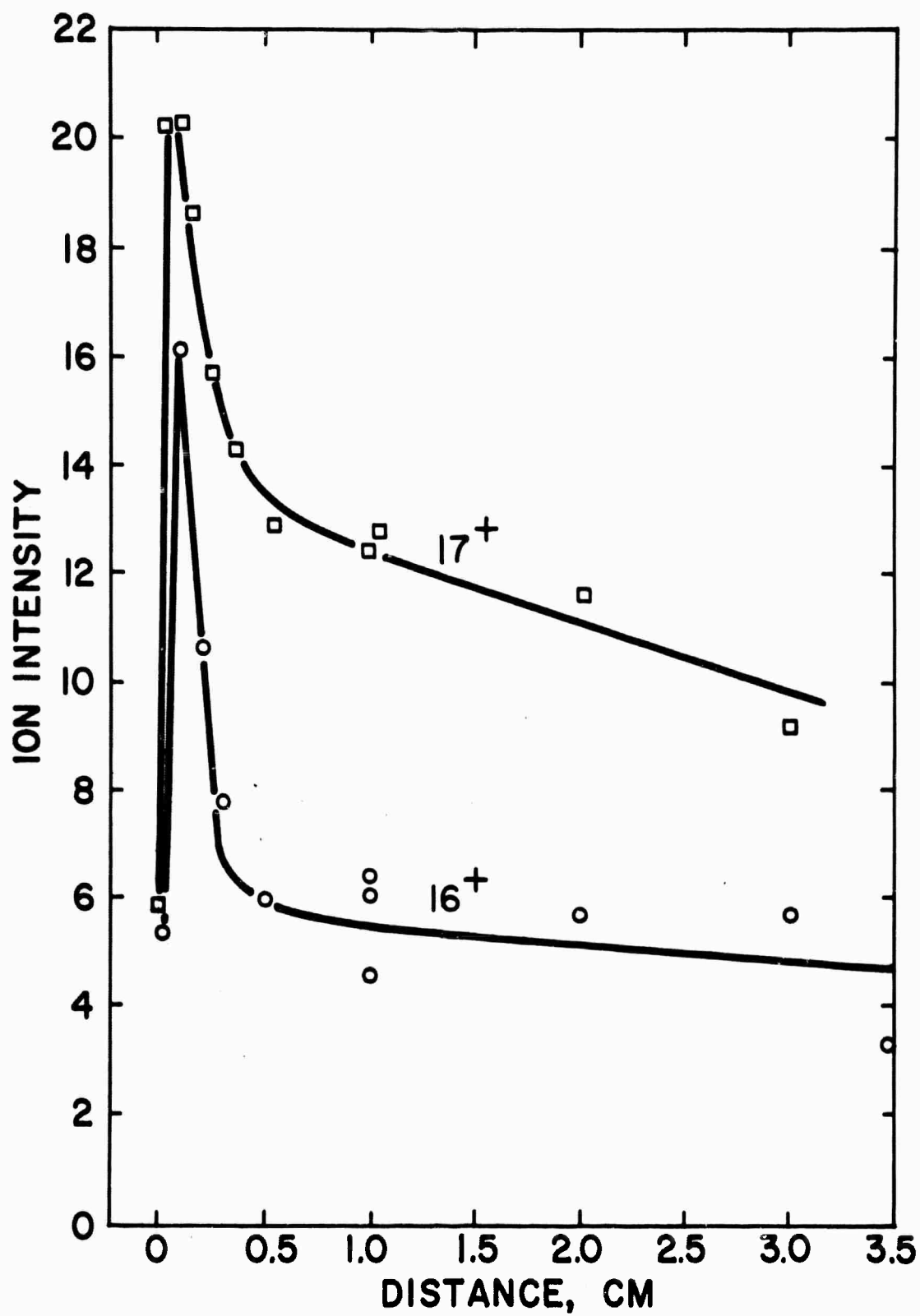
Fig. 3 - Oxygen Atom and Hydroxyl Radical Profiles in a Lean H_2-O_2 Flame Directly Sampled at 2540°K and One Atmosphere

TABLE IV

HYDROXYL RADICALS SAMPLED FROM SEVERAL ONE-ATMOSPHERE H₂-O₂-N₂ AND CH₄-O₂ FLAMES

H_2-O_2-N_2 AND CH_4-O_2 FLAMES

Flame Composition (Mole Ratios)				Adiabatic Flame Temp.	H_2O^+/OH^+		Calc.
H_2	CH_4	O_2	N_2	(°K)	50 ev.	20 ev.	H_2O/OH
	1	4		2845	2.5	8.3	4.0
4		1		2830	2.9	35.8	24.9
2		3		2720	2.6	11.9	6.5
2		1	2	2709	3.1	19.7	14.2
5		1		2627	3.3	52.3	66.7
	1	1		2611	3.2	37.3	64.0
2		4		2570	2.8	11.4	8.3
2		1	3	2524	2.8	21.7	26.6
2		1	4	2334	3.0	32.5	56.0
2		5		2330	2.8	14.6	15.7
	1	8		2330	2.5	9.8	13.1

TABLE V

EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR THE REACTION $H_2O + O \rightleftharpoons 2OH$ IN SEVERAL H_2-O_2-N_2 FLAMES AT ONE ATMOSPHERE

Flame Composition (Mole Ratios)			Adiabatic Flame Temp.	K_{eq} for $H_2O + O \rightleftharpoons 2OH$	
H_2	O_2	N_2	(°K)	Exptl.	Calculated
2	1	1	2889	0.50	0.52
2	3		2720	0.33	0.44
2	1	2	2709	0.50	0.43
2	4		2570	0.22	0.37

The agreement is good, showing that O and OH are equilibrated. The data of Table III show that neither O nor OH concentrations alone greatly depart from equilibrium. As with the O atom data, OH radicals were sampled more carefully from two flames on sheated burners: a 2-4 and a 5-1 H_2-O_2 flame. For both flames, results agreed with the torch results of Table III at the measured flame temperatures which were within 50°K of the adiabatic temperature. The OH profile appears in Fig. 3 for the 2-4 flame. The concentrations of both radicals peak sharply when the sampling orifice appears to just touch the reaction zone.

Some direct measurements of H atoms were made at 20 ev. in four flames varying from rich to stoichiometric. The H^+ results are considerably less reliable than the O and OH values because of the low sensitivity caused by the mass separation effect. Still, as shown in Table VI, in three out of four flames the equilibrium constant agrees with literature values to within a factor of two. Excess H atoms were observed, as expected, near the reaction zone. As yet no study of the H atom in sheathed burners has been made because of the extreme heating of the present thin orifices in these hot, H_2-containing flames.

TABLE VI

EXPERIMENTAL DETERMINATION OF THE DISSOCIATION OF H_2 IN
SEVERAL H_2-O_2-N_2 FLAMES AT ONE ATMOSPHERE

Flame Composition (Mole Ratios)			Adiabatic Flame Temp. (°K)	$1/2\ H_2 \longrightarrow H$	
				Exptl.	Calc.
H_2	O_2	N_2		K_{eq}	
3	1		3004	0.068	0.155
2	1	1	2889	0.10	0.112
4	1		2835	0.018	0.100
5	1		2627	0.025	0.043

In one very hot torch flame, an attempt was made to measure every species of even minor importance. Table VII shows the ion intensities observed at 20 ev., after correction for mass separation and normalization to the theoretical H_2O value. Even without corrections for relative cross sections, true flame temperatures, mass spectrometer transmission, or detector efficiency, the results reflect the expected composition.

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TABLE VII

RELATIVE ION INTENSITIES OBSERVED IN A ONE-ATMOSPHERE
H_2-O_2-N_2, 2-1-1 FLAME (T-2889°K) AT 20 EV. IONIZING ENERGY

Ion Observed	Per Cent	
	Exptl.	Calc.
H^+	0.75	3.2
H_2^+	2.25	8.8
O^+	0.42	1.3
OH^+	3.2	5.6
H_2O^+	(47.5)	47.5
N_2^+	14.7	29.9
NO^+	0.12	1.0
O_2^+	0.70	2.7

Results obtained from one other flame system are rather interesting. When a few per cent of either H_2S or SO_2 was added to a rich 5-1 H_2-O_2 flame, species profiles virtually identical to those shown in Fig. 4 were obtained. The initially very high concentrations of SO, S, and SO_2 and the late appearance of SH and SH_2 are noteworthy. Further study of this system should lead to new insight into the mechanisms of combustion of sulfur compounds. Similarly, in a lean 2-4 H_2-O_2 flame with SO_2 or H_2S added, the SO_2^+/SO^+ ratio was nearly constant through the flame and only slightly lower than for cold, pure SO_2. These observations agree with equilibrium calculations which show that SO_2 is the major species. It may be that, with more careful study of appearance potentials and fragmentation patterns, one can shed light on the postulated existence of an isomer of SO_2, perhaps with a peroxide bonding, believed to be formed in the early stages of the combustion of sulfur compounds.[18]

V. CONCLUSION

The sampling results presented in this paper show that at least some highly reactive species can be quantitatively sampled from 1-atm. flames. The departures from the literature of the measured values of equilibrium constants are virtually all within the estimated experimental error. Such success is to be expected on the basis of the calculated rate of the free jet expansion. For more precise work, more study is needed on flame-probe
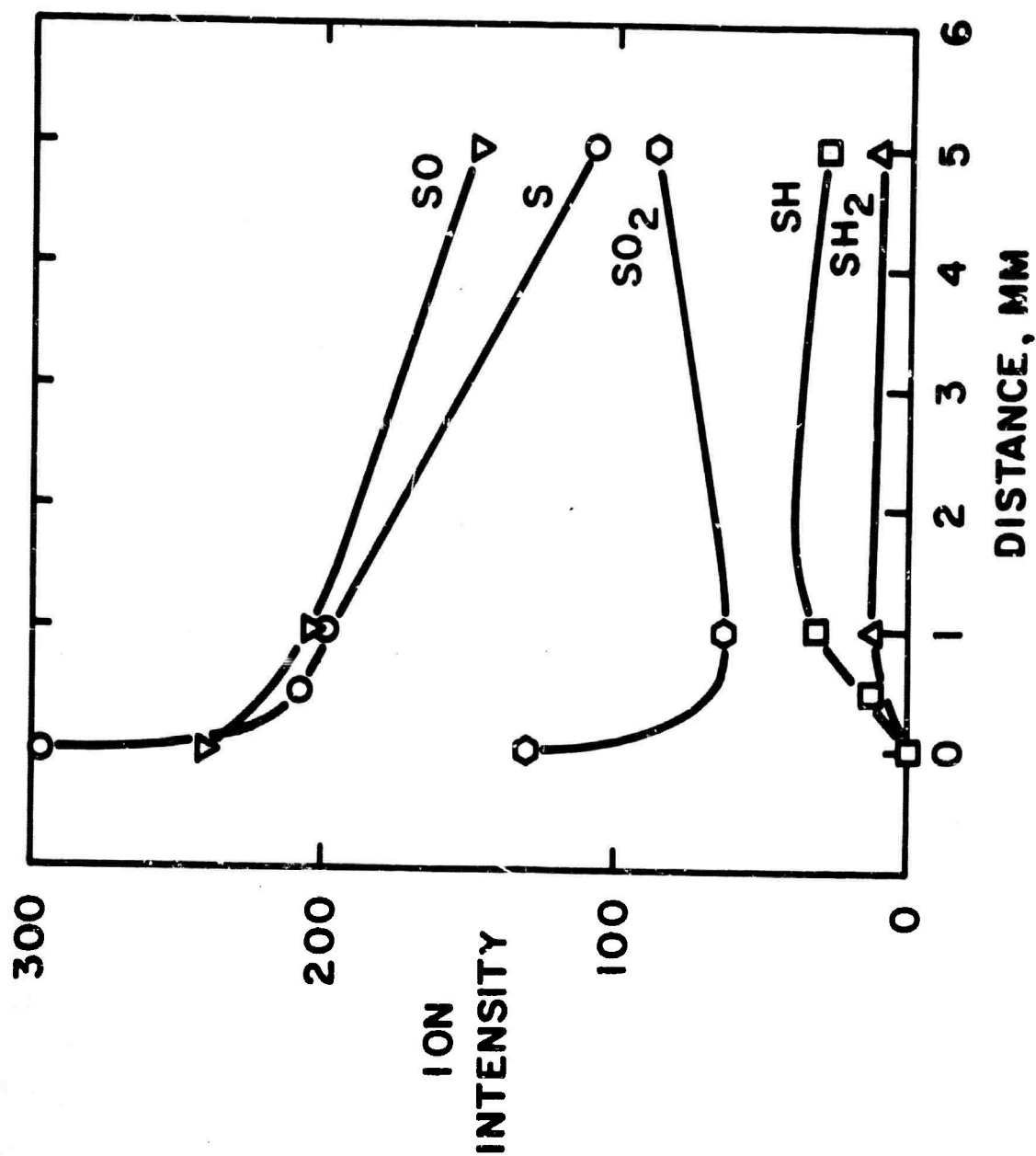
Fig. 4 - Sulfur-Containing Species Profiles in a Rich One-Atmosphere, H_2-O_2 Flame to Which a Few Per Cent of Either H_2S or SO_2 Had Been Added

i: ictions, orifice size effects, expansion dynamics, and a better under-
standing of the effect of temperature on the fragmentation processes.

Two major problems must be resolved before this flame sampling
technique can be extended to high-temperature, condensable species. One is
the mundane but troublesome problem of physical plugging of the cooled sam-
pling orifice by condensed phases of the material being sampled. This problem
can be reduced by the use of sufficiently large orifices and minumum metal
concentrations. This difficulty will not be encountered in situations in
which the sample and sampling orifice are in thermal equilibrium. The second
problem is that of the nucleation or partial condensation of species during
the expansion, particularly if the species are initially near saturation.
This area is being studied in a continuation of work reported earlier.[10]

Direct mass spectrometric sampling of high pressure sources should
be useful in many scientific and practical problems. Sampling of the reaction
zone of 0.01 to 0.1-atm. flames is now under way in order to study the kinet-
ics of the high temperature reactions of both combustion intermediates and
various other species. The extension of this direct sampling technique to
other relatively high pressure kinetic and equilibrium studies should also be
fruitful.

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Direct mass spectrometric sampling studies of one-atmosphere flames are
described. A simple model of the sampling process is summarized which
accounts for the effects and results obtained. Stable product analysis
and evidence for appreciable temperature dependence of fragmentation
patterns are shown. Quantitative sampling of the free-radicals H, O,
OH and Cl from the burnt gas region of one-atmosphere flames is demon-
strated, with direct observation of excess free radical concentrations
in the reaction zones of these flames.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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